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Electrochemical and photoelectronic studies on C_{60}-pyrrolidine-functionalised poly(terthiophene)

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ABSTRACT

A novel donor-acceptor poly(terthiophene) derivative bearing a C_{60} pendant was electropolymerizated from *N*-methyl-2-(2-[4,4′′-didecyloxy-2,2′;5′,2′′]terthiophen-3′-yl-ethenyl)fullero[3,4]pyrrolidine (TTh–C_{60}) solution. The electroreduction of TTh-C_{60} and poly(TTh-C_{60}) showed the presence of complex peaks related to fulleropyrrolidine reduction. The dual nature of these redox couples may be related to increasing Coulombic repulsion or coupling between C_{60} substituents. Electrochemical, X-Ray photoelectron spectroscopy (XPS), Ultra-Violet photoelectron (UPS) and UV-Vis spectroscopy also confirm the nature of poly(TTh-C_{60}). Electrochemical band gap of poly(TTh-C_{60}) is 0.63 ± 0.20 eV in TBAP electrolyte and propylene carbonate (PC) solution. Furthermore, we obtained the value of optical energy band gap (E_{opt} = 0.59 ± 0.03 eV), the transport energy band gap ($E_{g\ trans}$ = 1.17 ± 0.20 eV) and the exciton binding energy (E_b = 0.58 ± 0.20 eV) for poly(TTh-C_{60}). The ionization energy values (IE) were determined using UPS spectroscopy (IE = 4.92 ± 0.10 eV) and electrochemical investigations of the poly(TTh-C_{60}) polarized in TBAP/DCM (IE = 5.01 ± 0.10 eV) and TBAP/PC solution (IE = 4.95 ± 0.10 eV) demonstrating good coincidence of the value. The electrochemical method revealed, that the location of the Fermi level relative to the valence and conduction bands indicates p-type character of semiconducting poly(TTh-C_{60}). On the other hand photoemission spectroscopy manifests n-type behavior of examined sample. In turn, the UV-Vis result showed that the charge transfer (CT) between poly(TTh) and C_{60} unit can suggest, that these chromophores are not entirely independent.

1. Introduction

Fullerenes and their derivatives have been studied for its unique properties and potential applications as a ferromagnets [1], as a superconductors [2], in electro-optic devices [3] and medicinal chemistry [4]. The first evidence of the interest of fullerenes for photovoltaic (PV) applications resulted from the discovery of a highly efficient photoinduced electron transfer process from a photoactive semiconducting π-conjugated polymer to C_{60} [5,6]. The main problem of the use of fullerene-polymer blend is usually the chemical incompatibility of the components leads to undergo uncontrolled macrophase separation to form domains larger than the exciton diffusion length, which hinders the photoinduced charge separation and the charge transport in the composite material [7]. In order to overcome this problem and to obtain homogenous blend, modified fullerene derivatives were developed such as 1-(3-methoxycarbonylpropyl)-1-phenyl[6,6]methanofullerene (PCBM) [8]. It is worth pointing out that the exposure of polymer-PCBM blend to sunlight 'for a long time' causes macrophase separation of the donor–acceptor blend and in effect suppresses the photovoltaic performance [9,10].

To control the morphology and minimize the donor-acceptor macrophase separation, donor-π-acceptor "double cable" conjugated polymers were developed in which a π-conjugated semiconducting polymer (p-type cable) is covalently connected to fullerene units (n-type cable) [11,12]. The first example of a double cable polymer was reported in 1994, synthesized by electrochemical polymerization of bis(trimethylsilyl)methanofullerene,

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resulting in a polyacetylene derivative [13]. In turn, the first report of a "charm bracelet" poly(cyclopentabithiophene) structures with covalently bound C_{60} occurred in 1996 [14]. The cyclic voltammogram of the poly(cyclopentabithiophene) substituted methanofullerene showed three reversible one-electron reduction processes typical of C_{60} and anodic process, ascribed to the reversible oxidation of the conjugated backbone. The UV-Vis spectroscopy study, revealed a distorted conjugated chain with an effective conjugation length shorter than the unsubstituted polymer, but confirmed that the donor and acceptor moieties of the material basically retain their individual electronic and electrochemical properties. The particularly interesting property of π-conjugated polymer substituted by C_{60} is a low value of the energy band gap. A remarkable example has been described by Wudl and co-workers [15], where the electropolymerized double-cable poly(terthiophene) with the C_{60} units through a thieno[3,4-b]pyrazine bridge showed value of 0.7 eV. This indicates that to achieve low band gap is to employ electron-rich and electron-deficient units in a polymer as the donor–acceptor interaction could increase intramolecular charge transfer (ICT) [16,17].

The first results already showed that, the mutually independent ground-state electronic properties of the donor backbone and of the fullerene acceptor moieties can be provided by development of effective conjugation length. For example, two terthiophenes were electrochemically polymerized carrying a fullerene cage via an acetylenic bridge [18]. While one of them was unstable due to the presence of a reactive hydrogen on the fullerene moiety, the latter was electroactive and stable upon both anodic and cathodic cycling processes, and showed an absorption spectrum extending to above 700 nm.

Another approach is use of using flexible spacers of the proper length "isolated" in order to prevent ground-state interactions [19]. The examples are polythiophenes covalently bound to fullerenes were poly(bithiophene) with a C_{60} group attached at an internal β-position of one thiophene ring via an alkyl spacer [20,21] or phenyl polyether linker [22,23]. For the latter, light-induced electron spin resonance (LESR) experiments performed under light excitation confirmed the photo-induced formation of the poly(thiophene) polaronic state and C_{60} radical anion. These results thus provided clear evidence for a long-lived and mobile charge-separated state in this electrogenerated polymer [23].

However, oligothiophenes covalently bound to fullerenes, have received little attention [24–26]. The examples are: a fullerene-oligothiophene-fullerene triads described by van Hal [27]; linear or branched oligothienylenevinylenes bearing one to three terminal C_{60} groups [28,29], [60]fullerene-oligo(thienylene–ethynylene) [30] or diketopyrrolopyrrole-oligothiophene/fullerene dyads [31]. These last results indicate that the alkyl side chain have an important influence on π-π stacking in the solid state, consequently these groups effect performance of photovoltaic devices. The dyads and triads capable of intramolecular electron transfer also enhance geminate carrier recombination too. The synthetic strategies toward fullerene derivatives able to self assemble with suitably designed conjugated polymers should be considered as an alternative to covalently bound double-cables, too. To this end, self-assembly strategies based on electrostatically driven or other key–lock interactions should be possible [32].

To successfully apply a donor-π-acceptor double-cable poly(terthiophenes) bearing C_{60} into organic electronics, the knowledge of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and hence band gap energy (E_g) is crucial [33]. It is important to stress that one cannot measure directly the molecular orbital energies, but rather ionization energy (IE) and electron affinity (EA). The difference IE–|EA| is called the electrochemical band gap. Two conventional methods to ascertain IE energy is Ultra-Violet photoelectron spectroscopy (UPS) [34,35] and cyclic voltammetry (CV) [36]. UPS determines the ionization energy of a molecule on the surface of material. In turn, solution-based CV experiments determine the onset potential (E_{onset}) of oxidation referred to formal potential ($E^{o'}$) or half-wave potential ($E_{1/2}$) of the ferrocene/ferrocenium (Fc/Fc^+) couple. This means that often electrochemical measurement in various solutions differs from measurements in solid state by UPS. Generally, the reference point is peak position of Fc/Fc^+ and just the main problem is convert the value of the electrochemical scale into one, referred to vacuum. The most common examples of IE calculation can be obtained from equations: $IE = ([E_{onset}ox - Eo'(Fc/Fc+)] + 4.8)(eV)$ [37,38]; $IE = ([E^{ox}_{onset} - E_{1/2}(Fc/Fc+)] + 5.1)(eV)$ [39–41]

The primary intent of this work was investigate the electrochemical and photoelectronic properties of new terthiophene bearing covalently attached C_{60} units (Scheme 1-c) and comparison its of the analogous monomer without alkoxy groups described in the earlier publication [42]. The fullerene side-groups are thought to impede the ability of the backbone polymers to crystallize, resulting in limited hole carrier mobility. The electron-donating groups containing heteroatom such as alkoxy placed in the 3,4 position in heteroclic ring are shown to decrease the band gap by raising the level of the HOMO levels, leading to low oxidation potential and a stable conducting state. The [60]fullerene derivatives with long alkyl or alkoxy chains may cause the self-assembled of the polymer [43]. In-plane transport is expected to be favorable in the case of photovoltaic devices when the active layer is sandwiched between two electrodes.

The electrochemical UV–Vis and UPS studies were performed to verify the correlation between experimental values characterized of poly(TTh-C_{60}) (e.g. ionization energy, band gap energy).

2. Experimental

2.1. Chemicals and materials

2.1.1. Synthesis and materials characterization

The fullerene-functionalised terthiophene monomer, N-methyl-2-(2-[4,4″-didecyloxy-2,2′;5′,2″]terthiophen-3′-yl-ethenyl)fullero[3,4] pyrrolidine (TTh–C_{60}) (Scheme 1-c), was synthesized via 2+3 dipolar cycloadditon (Prato reaction).

3′-Formyl-4,4″-bisoctyloxy-[2,2′:5′,2″-terthiophene] (**a**) was synthesized according to literature procedures [44], the other chemicals were commercially available and used without further purification unless stated differently.

3′-(2-formylethenyl)-4,4″-bisoctyloxy-[2,2′:5′,2″-terthiophene] (**b**): Aldehyde (**a**) (1.18 g, 2.0 mmol), 18-crown-6 (52 mg, 0.2 mmol) were dissolved in benzene (75 mL), brought to reflux then (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide (0.86 g, 2.0 mmol) with anhydrous, finely powdered, potassium carbonate (0.18 g, 1.30 mmol) was added every 2 h for 6 h (3x). Afterward the reaction mixture was cooled down and filtered through a pad of silica using chloroform as an eluent. The solvents were removed under reduced pressure at 50°C and the remaining solid was dissolved in a mixture of tetrahydrofuran (50 mL) and chloroform (13 mL). The concentrated hydrochloric acid (6.5 mL) was added and the resulting mixture was vigorously stirred for 45 minutes. The acid was neutralized with concentrated ammonia and the organic phase after dilution with dichloromethane (50 mL) was separated, dried over magnesium sulphate and evaporated to dryness under reduced pressure at 50°C. The crude product was purified on silica using dichloromethane as eluent to give product as yellow viscous oil which solidified with time.

Yield: 83%; ^1H NMR (500 MHz, $CDCl_3$, TMS):δ 9.68 (d, 1H, J = 7.9 Hz, CHO), 7.70 (d, 1H, J = 16.0 Hz, CH1), 7.30 (s, 1H, Th-H4′), 6.88